J. Pure Appl. & Ind. Phys. Vol.3 (2), 178-185 (2013)

The Current Study of Rare Earth Magnetism and Evaluation of Magnetic Structure of Holonium

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(Received on: March 18, 2013)

ABSTRACT

Magnetic properties of the rare earth metals differ, in many aspects, from those of other metals in the periodic table of elements. A most amazing effect arises, when several electrons are put together and are treated as one many-particle system. By virtue of their Fermionic character, an additional interaction occurs named as Exchange. This interaction is a consequence of the fact, that two identical particles cannot be distinguished in quantum Physics. Note that there is a crucial difference between rare earth metals and transition metals although both species possess open inner shells, 4f shells in the case of rare earths, and 3d, 4d or 5d shells respectively in the case of transition metals. The latter are rather delocalized and their wave functions reach far enough, to overlap with the respective neighboring wave functions whereas 4f electrons of rare earth ion cores are fully localized. Exchange interaction between the localized spins of 4f shells is an indirect one, being mediated by the 6s and, if available, the 5d conduction electrons. To point out the prominent part of rare earths among the magnetic metals, a new approach with electronic structure of the rare earth 3+ ion cores and indirect exchange between their localized magnetic moments in the metal is described. Finally, the magnetic structure of holmium is discussed. Where it has been found that in rare earth metals, conduction electrons play the crucial part in magnetic ordering & the structure of the localized magnetic moments matches experimentally as well as theoretically.

Keywords: Rare earth, Delocalization, Magnetic Moment, Exchange Interaction.

1. INTRODUCTION

Magnetic properties of the rare earth metals differ, in many aspects, from those of other metals in the periodic table of elements. In metallic elements leaving magnetic ordering aside, there may be four possible contributions to magnetic susceptibility in a metal: Ion cores contribute, depending on their electronic structure, with diamagnetic and in some cases with paramagnetic moments[1], Conduction electrons always contribute with both[2]. In a rough classification, metals can either have closed or open ion-core electron shells. Those with open core-shells can be further subdivided into transition metals with open d shells, and lanthanides and actinides respectively having open f shells[3]. In this strict definition, the lanthanides and actinides would only range from cerium(i.e. thorium) to thulium (i.e. mendelevium).

Lanthanum, yterbium and lutetium as well as actinium, nobelium Lawrencium have filled shells. Nevertheless, in Mendeleev's periodic table[4] they are accounted for the lanthanides and actinides due to their very similar chemical properties with respect to magnetism, they differ dramatically. The fraction of transition metals includes the elements between third and tenth period. Copper, silver and gold have closed d shells, and thus do not belong to the transition metals according to their magnetic properties. They also owe their prominent position only to their valence-electron configuration. Before the magnetic properties of rare earth metals are discussed, the crucial difference to the transition metals shall be pointed out. Both species possess open inner shells, 4f shells in the case of rare earths, and 3d, 4d or 5d shells respectively in the case of transition metals. The latter are rather delocalized. Their wave functions reach far enough, to overlap with the respective neighboring wave functions. The term inner shell is somewhat misleading in the case of the transition metals. Magnetic ordering[5] in such d-systems is contributed to exchange interaction between the spins of these overlapping shell.

The Crystal field splitting is negligible against the separation of the spin-multiplet states. For the 4f levels there is no overlap with the neighborhood, and the states of the free atom remain largely intact. Exchange interaction between the localized spins of 4f shells is an indirect one, being mediated by the 6s and, if available, the 5d conduction electrons. To point out the prominent part of rare earths among the magnetic metals, a new approach with electronic structure of the rare earth 3+ ion cores and indirect exchange between their localized magnetic moments in the metal is described. Finally, the magnetic structure of holmium is discussed.

2. MAGNETISM IN RARE EARTH METALS

The rare earth metals feature a rich variety of magnetic ordering schemes. They owe their prominent position among the magnetic elements to their

localized magnetic moments, which interact indirectly via conduction bands. Within their period, the magnetic moments of the rare earth atoms are tuned with increasing atomic number. The interplay of local magnetic moments, spatial electron distribution and periodic exchange coupling nurtures[6] exotic magnetic structures, culminating in the cone-helical ordering of holmium. As exchange interaction is strongly influenced by the shape of the Fermi surface, those extraordinary magnetic properties are also reflected in the electron transport properties. Optical properties can be investigated at different temperatures. Note that in contrast to the state of affairs within transition metals the 4f electrons of rare earth ion cores are fully localized and surrounded by the filled 5s and 5p shells they are well screened from the surrounding lattice.(see figure 1).

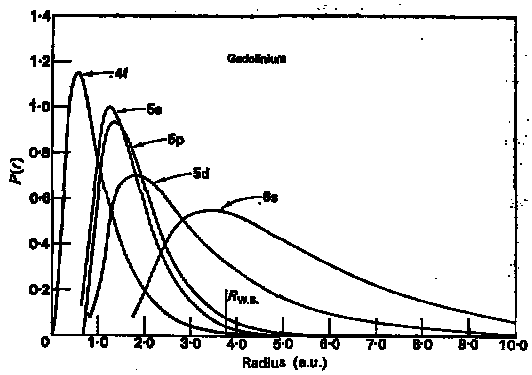

Figure 1: Radial distribution of the electronic wave functions in gadolinium[11]. The open 4f shells are screened by the closed 5s and 5p shells. $R_{W.S.}$ is the half inter-ionic distance in the metal. Thus there is a wide overlap between the neighboring 5d and 6s wave functions.

2.1 3+ Iron Cores

In the metallic state rare earths use to occur as trivalent ion cores, each of the atoms contributing with three electrons to the metallic bonding. One of the inner 4f electrons is promoted to a band state and participates in the metallic bonding, together with the two 6s (and the 5d, if present) electrons. Exceptions are cerium (*C e*4+), europium(*Eu*2+) and ytterbium (*Y b*2+). They step out of the line, as a completely empty or a completely filled 4f shell is energetically most favorable (Hund's Rules). For magnetism the closed inner shells are of no importance, as their net magnetic moments cancel out. Valence electrons only account for a small fraction of magnetic susceptibility, although they are the essential mediators of exchange in the ordered states. Thus, the 4f electron shells are protagonists in terms of the magnetic moment. Their occupation with increasing atomic number within the period of the rare earth elements perfectly displays the validity of the Pauli principle and Hund's rules. The total angular momentum of the 4f electrons can be determined according to Russel-Saunders coupling. All orbital angular momenta lj all electrons are coupled via Coulomb interaction to a total orbital momentum *L*L, while all spins Sj are separately coupled by exchange interaction to the total spin momentum S. The degeneracy of the different possible J multiplets is lifted. In the case of a less than half-filled shell the multiplet with the lowest quantum number J has the lowest energy (i.e. $J = L - S$). For more than half-filled shells it is the other way around (i.e. $J = L + S$) [7]. Table 1 shows the respective quantum numbers for the rare earth metal series. The Land´e factor in the case of Russel-Saunders coupling is[8]:

g=3/2+S(S+1)-L(L+1)/2J(J+1)

The energetic distance of the lowest lying multiplet to the next higher one is large. At room temperature only the ground state is occupied .Thus the contribution of Van Vleck paramagnetism to the total paramagnetic moment, i.e. the admixture of the ground state multiplet with higher ones, is negligible (exceptions: samarium and europium [9]. When the total angular momentum of the shell is known, the paramagnetic moment of the ion is

$$\mu = g\mu_B J \text{ i.e. } |\mu| = g\mu_B\sqrt{J(J+1)}$$

In the case of heavy rare earth metals, the theoretically predicted values are only slightly lower than the measured ones. This is due to a contribution of the conduction elec trons. For high temperatures, i.e. in the paramagnetic regime, the magnetic susceptibility of rare earth metals can be well estimated by a Curie-Weiss law[10].

$$X = N\mu^2 Bg^2 J(J+1)/3K_B(T-\theta)$$

Here, N is the number of atoms, μB is the Bohr magneton, kB is the Boltz- mann factor, T is the temperature, and θ is the Curie temperature.

2.2 Magnetic Interactions

The importance of exchange interaction for the ordering of spin magnetic moments has shown that in contrast to the transition metals there is no overlap of the magnetic 4f states between neighbors and nevertheless ordering occurs. In rare earth magnetism the conduction electrons play a chief part in mediating exchange interaction between the magnetic ion sites.

Table 1: Quantum numbers and Land*e* factors for the rare earth 3+ ions. The experimental data for the paramagnetic magnetization per atom in units of μB for the heavy rare earths coincide well with the theoretical values[8].

$4f^n$	3+ Ion	L	S	J	g	$\frac{G}{g(j(J+1)^{1/2}}$	$_{para}\mu^{exp}$ (μ_B)
0	La	0	0	0			
1	Ce	3	1/2	5/2	6/7	2.54	2.51
2	Pr	5	1	4	4/5	3.58	2.56
3	Nd	6	3/2	9/2	8/11	3.62	3.4
4	Pm	6	2	4	3/5	2.68	
5	Sm	5	5/2	5/2	3/7	0.85	1.74
6	Eu	3	3	0			
7	Gd	0	7/2	7/2	2	7.94	7.98
8	Tb	3	3	6	3/2	9.72	9.77
9	Dy	5	5/2	15/2	4/3	10.65	10.83
10	Ho	6	2	8	5/4	10.61	11.02
11	Er	6	3/2	15/2	6/5	9.85	9.9
12	Tm	5	1	6	7/6	7.56	7.61
13	Yb	3	1/2	7/2	8/7		
14	Lu	0	0	0			

Rare Earth Band Electrons

The 5d and 6s electron states of the rare earth metals have a considerably higher energy, than the 4f states (ΔE approximately 10 eV). The latter lie within the ion core, well screened by the closed

5s and 5f shells. Figure 1 shows the position probability of the respective states in the case of gadolinium. The marked atomic radius implies a wide overlap for the outer shells, which results in the formation of a broad s-d conduction band. As already noted, for the heavy rare earth metals it was assumed, that one of the 4f electrons is promoted into a d state. This assumption is justified by a multitude of experimental results from crystal-structure, melting-point or heat-of-sublimation measurements. Early band structure calculations[11] do not account for any influence of 4f states on conduction bands. More recent publications include the 4f states in the band structure, and model the splitting of the 4f states into fractions of localized and band electrons. They allow ab initio calculation of the contribution of 4f levels to valency. The results predict a hybridization between 4f and 6s levels. This can lead to extraordinary high densities of states just above the Fermi level. This increased density of states was confirmed by the far-infrared measurements, presented in this work.

RKKY Interactions

Indirect (RKKY) exchange in rare earth metals acts in two steps. A localized spin magnetic moment polarizes the surrounding conduction electron spins and they, in turn, polarize the next-neighbour local spin moments. Exchange interaction between the 4f and the band electrons (s-f or s-d interaction,[12,13], is promoted by the large overlap of the respective wave functions, and plays a fundamental part also in other physical problems like the Kondo effect. Ruderman and Kittel[14] first developed the idea of indirect exchange interaction for the coupling of nuclear magnetic moments in metals. Kasuya and Yosida applied their considerations on rare earth and transition metal systems[15].

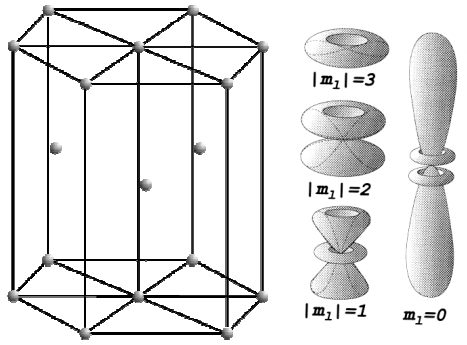

Figure 2: Hexagonal close packed crystal structure of holmium and the anisotropic charge cloud of the 4f electron niveaus[16].

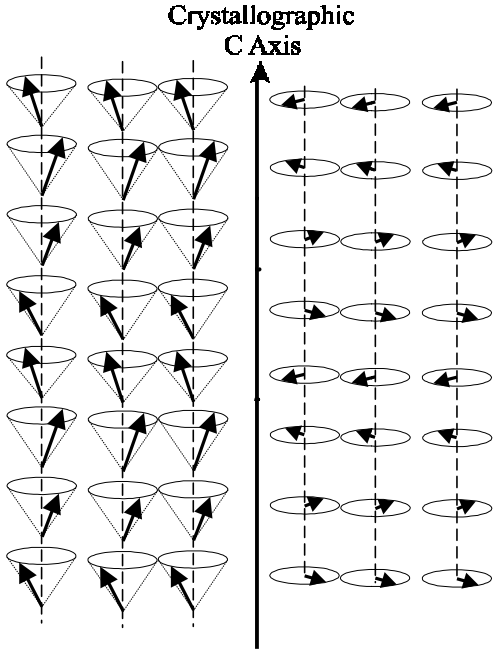

Figure. 3: Below 133 K holmium orders in a basal-plane antiferromagnetic helical structure (right).The ferro-cone helix structure shapes below 20 K (left).

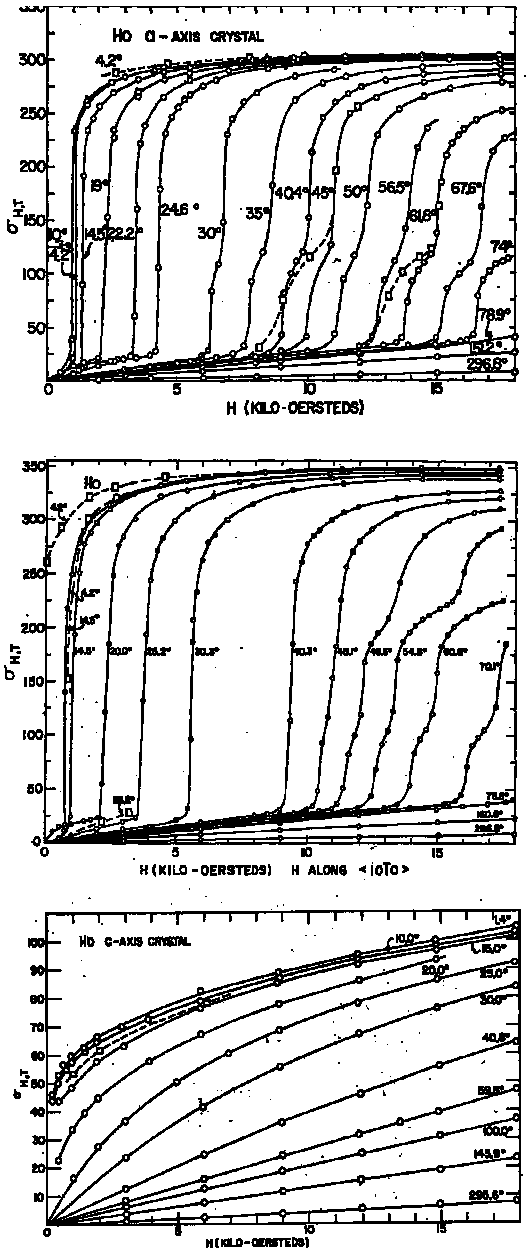

Figure 4: Magnetization of holmium in the three directions of the hcp crystal lattice at different Temperatures[54]. From top to bottom: (1000), (0110), and (0001)

Magnetic Structure of Holmium

All heavy rare earth metals form a hexagonal close packed (hcp) lattice (2). They show an amazing variety of magnetic structures. The interplay of oscillating, indirect exchange and sstructured Fermi surface leads to a strongly anisotropic magnetic interaction[17,18]. Figure.2 shows the 4f-electron charge clouds in a free ion. They constitute a pronounced electric multipole. The electrostatic crystal field of hexagonal symmetry alters these polar orbitals and, via spin-orbit coupling, strongly promotes exchange anisotropy. Oscillations of RKKY exchange interaction with ionic distance allows for fer romagnetic, as well as antiferromagnetic ordering. ready above the Neel temperature as for example transport measurements (heat and electric conduction) reveal. The antiferromagnetic spin structure is a basal plane helix.

RESULTS AND DISCUSSION

As shown in figure 3, all spins are aligned within each basal plane. When propagating towards c-axis direction (perpendicular to the basal planes), the collective spin direction is turned from plane to plane for a certain angle. Just below N´eel temperature this turning angle is about 50◦ and it decreases to about 30◦ at 4.2 K. The helical structure tends to be commensurable with the lattice. At 4.2 K it has a periodicity of 12 planes. At 20 K there occurs a second-order phase transition to ferromagnetic order- ing. The basal plane arrangement stays the same but all moments are tilted out of the plane to form a ferro-cone helix. The opening angle of the cones

is about 80◦ (see figure 3). The out-of-plane component of the magnetic moment per atom at 4.2 K is 1.7 μB while the in-plane component takes a value of 9.5 μB. Easy axis is the in-plane b-direction (1010). Application of a field yields a saturation magnetization in that direction of 10.34 μB. It is slightly larger, than the value expected from the ionic moment (gJ = 10). Application of a field in-plane but deviating from b-axis direc- tion only enforces an alignment along the latter at high enough fields. Thus the measured saturation magnetization is reduced then. The c-axis is the hard axis of magnetization. Figure 4 shows magnetization measurements of Strandburg, Legvold, and Spedding. The magnetic field direction was (1000), (0110), and (0001).

In rare earth metals, conduction electrons play the crucial part in magnetic ordering. The structure of the localized magnetic moments was extensively studied by neutron scattering experiments[18]. The ”deep-in” band struture was explored by photoemission[19]. Both the studies shows similar results to that of above magnetization properties.

ACKNOWLEDGEMENT

We are very thankful to Dr. Nidhi Sharma Lecturer HPES for her guidance and Support.

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